

Effect of Nanoclay Loading on the Hardness Property of Epoxy Composites

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Abstract

This study examines the influence of nanoclay loading on the hardness properties of epoxy composites. Nanocomposites were fabricated using varying weight percentages of nanoclay and epoxy via the hand layup method with an open mould. Mechanical characterisation was carried out using a Rockwell hardness tester, while the dispersion and morphology of nanoclay particles within the epoxy matrix were analysed using Scanning Electron Microscopy (SEM). The composite containing 4 wt.% nanoclay (nanoclay-to-epoxy ratio of 4:96) exhibited the highest hardness value of 109.60 HRA, representing a 65% improvement over the control sample (neat epoxy). The results demonstrate that the incorporation of nanoclay significantly enhances the hardness of epoxy, with hardness values increasing proportionally with nanoclay content up to an optimum level. Beyond this saturation point, a decline in hardness was observed, attributed to particle agglomeration and poor interfacial adhesion between the nanoclay and the epoxy matrix. Overall, the findings establish nanoclay as an effective reinforcement material for epoxy polymers where improved hardness is required.

Keywords: Nanotechnology, Nanocomposite, Epoxy, Nanoclay, Hardness and SEM

INTRODUCTION

This research investigates the effect of nanoclay loading on the hardness properties of epoxy-based materials. Hardness is generally defined as the resistance of a material to localised plastic deformation induced by mechanical indentation (Parida *et al.*, 2023). It is typically associated with strong intermolecular bonding at the macroscopic level (Lam, 2020). As a mechanical property, hardness enables a material to preserve the integrity of its surface under both static and dynamic loading. It also represents the resistance offered by pure or treated compounds against indentation on their surfaces (Al-Shawi *et al.*, 2021). Hardness measurements are commonly determined through indentation techniques such as the Rockwell test, which evaluates hardness by measuring the depth of penetration of an indenter under a major load relative to the penetration caused by a minor preload.

The hardness value of a material depends not only on its intrinsic characteristics but also on the testing method employed (Badaruddin and Samnur, 2024). The incorporation of reinforcement materials into polymer matrices is a widely adopted strategy to enhance hardness and other mechanical properties (Kusmono *et al.*, 2023). For example, the addition of particulate fillers into a material's structure can occupy lattice positions, thereby improving its hardness (Badaruddin and Samnur, 2024).

Polymers serve as essential matrix materials in the fabrication of advanced composites. Composites

generally consist of a stiffer, stronger phase, such as fibres or particles, embedded within a continuous matrix, which acts as the load transfer medium. In complex loading conditions, the matrix may also bear transverse loads. Typically, the matrix is more ductile than the reinforcement phase, thereby imparting toughness while also shielding the reinforcement from environmental degradation during processing and service (Sawsan *et al.*, 2023).

Polymeric composites have become integral to modern materials engineering, gradually replacing conventional materials in many structural and functional applications due to their advantageous properties, including high specific strength and stiffness, lightweight nature, wear resistance, corrosion resistance, high fatigue strength, low thermal expansion, ease of processing, and long service life (Takim and Okeoma, 2023). Their relatively low density, combined with enhanced strength compared to traditional alloys, has made them indispensable in material technology (Jojibabu *et al.*, 2020). Furthermore, fibre-reinforced, filler-reinforced, and particle-filled polymer composites are increasingly used in diverse industrial applications (Sawsan *et al.*, 2023).

Polymer matrices reinforced with micro- and nanofillers have received significant attention due to their high strength-to-weight and stiffness-to-weight ratios. Particulate composites, in particular, offer excellent durability while maintaining lightweight and design flexibility (Rajak *et al.*, 2023). Among

thermosetting polymers, epoxy resins are among the most widely utilised due to their superior mechanical and thermal properties (Al-Shawi *et al.*, 2021). Their good adhesion to fillers and fibres enhances stiffness and dimensional stability (Sawsan *et al.*, 2023). Other advantages include excellent corrosion and chemical resistance, thermal stability, high compressive and tensile strength, impact resistance, high hardness, low shrinkage, and low creep (Takim and Okeoma, 2023). Unlike many other polymer resins, epoxy maintains its properties in aggressive solvent environments (Sawsan *et al.*, 2023).

Nanocomposites share the same fundamental structure as conventional composites, differing mainly in the size of the reinforcement phase, which is typically in the nanometre range (Rajak *et al.*, 2023). The transition from micro- to nanoscale fillers significantly enhances the reinforcing effect. Due to their high surface area, nanoparticles improve interfacial bonding within the polymer matrix, leading to superior mechanical performance (Al-Shawi *et al.*, 2021). Epoxy nanocomposites often contain inorganic particles ranging from 1 to 100 nm uniformly dispersed within the epoxy matrix (Sawsan *et al.*, 2023). Such nanosized fillers reduce the likelihood of defects while maximising load transfer efficiency, resulting in enhanced mechanical properties (Belguri *et al.*, 2021).

The effectiveness of polymer nanocomposites depends on several factors, including filler type, dispersion quality, interfacial adhesion, and processing methods (Al-Shawi *et al.*, 2021). Common fabrication techniques include solution mixing, in-situ polymerisation, dry mixing, and melt mixing. However, nanoparticle agglomeration remains a critical challenge, which can be mitigated through low nanoparticle loading (Rajak *et al.*, 2023).

Nanoclays, a class of fine-grained crystalline minerals with high aspect ratios and nanoscale dimensions, are particularly attractive as polymer reinforcements (Jojibabu *et al.*, 2020). Their ability to undergo surface modifications and delaminate into lamellae structures has been widely exploited in composite development (Sawsan *et al.*, 2023). Nanoclays have been successfully incorporated into polymers to improve mechanical properties, gas barrier performance, solvent resistance, thermal stability, and flame retardancy (Al-Shawi *et al.*, 2021). Nevertheless, achieving homogeneous dispersion often requires pre-exfoliation due to their high surface area (Takim and Okeoma, 2023). Ultimately, the performance of nanoclay-reinforced composites is determined by the structural integrity of both the nanoclays (Parida *et al.*, 2023) and

the polymer matrix (Lam, 2020), as well as the degree of nanoclay distribution (Badaruddin and Samnur, 2024) and the strength of polymer–nanoclay interactions (Takim and Okema, 2023).

MATERIAL AND METHODS

Material

The nanoclay employed in this study possessed a particle size of ≥ 20 nm, an elastic modulus ranging from 10 to 400 GPa, and a density of 1.72 g/cm^3 (Product Code: 682608-500G). The epoxy matrix was formulated using Araldite LY 506 resin, which has a specific gravity of $1.15 - 1.20 \text{ g/cm}^3$. The curing agent utilised was Aradur HY 951 hardener, with a specific gravity in the range of $0.97 - 0.99 \text{ g/cm}^3$. In addition, polyvinyl alcohol (PVA) was applied as the mould release agent to facilitate demoulding of the composites.

Methods

Table 1: Shows the Percentage of Compositions of Nanoclay/Epoxy Composites

Composite	Epoxy (wt. %)	Nanoclay (wt. %)
1	100	0.00
2	99	1.00
3	98	2.00
4	97	3.00
5	96	4.00
6	95	5.00
7	94	6.00
8	93	7.00

Nanoclay/ Epoxy Composites Fabrication Method

Nanoclay/epoxy composites were prepared with varying weight compositions of 100:0 (control), 99:1, 98:2, 97:3, 96:4, 95:5, 94:6, and 93:7 wt.% (epoxy:nanoclay). Fabrication was carried out using the hand layup technique with open moulds. Before casting, the moulds were thoroughly cleaned and coated with a mould release agent to facilitate easy removal of the cured composites.

For each composition, the required weight of epoxy resin was accurately measured and transferred into a beaker. The corresponding weight of nanoclay was then added to the resin. The mixture was mechanically agitated using a high-speed motorised stirrer operating at 1000 revolutions per minute (rpm) for five minutes to ensure preliminary dispersion of the nanoclay particles. Subsequently, the appropriate quantity of epoxy hardener (Aradur HY 951; specific gravity $0.97-0.99 \text{ g/cm}^3$) was measured and added to the same beaker.

Agitation was continued for a further five minutes to achieve a uniform mixture.

The homogeneous mixture was carefully poured into the prepared moulds and allowed to cure under ambient conditions overnight. After curing, the composites were demoulded and labelled according to their respective compositions. This procedure was repeated for all weight percentages listed in Table 1.

Hardness Property Testing Method

The hardness properties of the nanoclay/epoxy composites were evaluated experimentally using a Rockwell hardness tester (Model No. 5019, Serial No. 01554), in accordance with DIN 53505, EN ISO 868, ASTM D2240, and ISO 7619 standards. The Rockwell hardness tester employed in this study was manually operated and equipped with the following specifications: a preliminary test force of 98.07 N (10 kgf), additional test forces of 490.3 N, 882.6 N, and 1373 N (50, 90, and 140 kgf, respectively), and corresponding total test forces of 588.4 N, 980.7 N, and 1471 N (60, 100, and 150 kgf, respectively). Test force selection was achieved through an external dial with an automatic zero-setting gauge.

For testing, composite specimens were prepared in a square geometry with dimensions of $10 \times 10 \times 3$ mm. Each specimen was subjected to hardness measurement under the prescribed load conditions, and the results were recorded accordingly.

RESULT AND DISCUSSION

Figure 1 shows the Rockwell hardness value of all the developed composites. It was observed that the incorporation of nanoclay particles/fillers into the epoxy matrix showed significant improvement in the value of hardness of the composites. An increase in hardness values represents the ability of the composites to stand more firmly to local surface deformation compared to the unfilled composite (Nikalje, 2024).

An increase in hardness may be due to the nanoclay fillers having higher hardness than pure epoxy resin (Parida *et al.*, 2023). The finding supports those of (Kusmono *et al.*, 2023), which recorded that a minute percentage of nanoparticles has the ability of enhancing greatly enhance the mechanical properties of polymers. It may also be due to the increased surface area of the nanoclay filler in the epoxy matrix (Lam, 2020). The hardness values increased with an increase in filler loading up to 4 % nanoclay filler loading, where it attained optimum hardness (109.6 HRA), after which it began to decrease gradually with additional increase in

filler loading. The increment in hardness can be attributed to the uniform and proper distribution of the nanoclay in the composite structure (Namdev *et al.*, 2023).

The increment could also be due to good interfacial adhesion and bond strength achieved between the nanoclay fillers and the epoxy matrix (Nadia *et al.*, 2015) or the nanoparticles might have imposed better resistance against epoxy segment motion under indentation (Ranganatha *et al.*, 2013). The increase in nanoclay loading leads to the improvement in the hardness property of the composites as observed in composites 2 to 5 until the optimum filler loading was reached (saturation point).

It can be said that below and up to 4 wt. %, the nano particles were very proficient to fill up the intermolecular pores (spaces) in the epoxy, thus, resulting in a harder and more rigid composite material (Nikalje, 2024).

Adding more nanoclay filler beyond the saturation point caused non-uniform dispersion and agglomeration/aggregation of nanoparticles caused by the nanometer-sized nanoclay particles, which resulted in a reduction in the hardness property (Kusmono *et al.*, 2023) of the nanoclay-filled nanocomposites beyond the optimum 4 wt. % filler loading (Namdev *et al.*, 2022).

This is understandable since, as the volume fraction of filler increases, the point is reached where particles are mutually in contact within the matrix. Beyond this point, stress is transferred across the material predominantly via (hard) particle-particle interactions. This results in a non-linear dependence of hardness with filler content (Abdulrahman *et al.*, 2018). The decrease in the hardness values observed in composites 6, 7 and 8, i.e. composites with filler loadings above 4 wt. % nanoclay content, may also be attributed to poor interactions between the matrix and nanoparticles. Composite 5 with 4.94 wt. % nanoclay/epoxy composition showed maximum/optimum hardness (109.6 HRA), i.e. making it the overall best (hardest) composite fabricated.

The least hardness value of 31 HRA was obtained from composite 1 (control sample with zero filler) with 100 wt. % epoxy, which implies that epoxy, just like other polymers, should be reinforced to achieve a better hardness value (Nikalje *et al.*, 2024). It is important to note that hardness is also influenced by the specific composition and structure of the organic matrix (Rajak *et al.*, 2023).

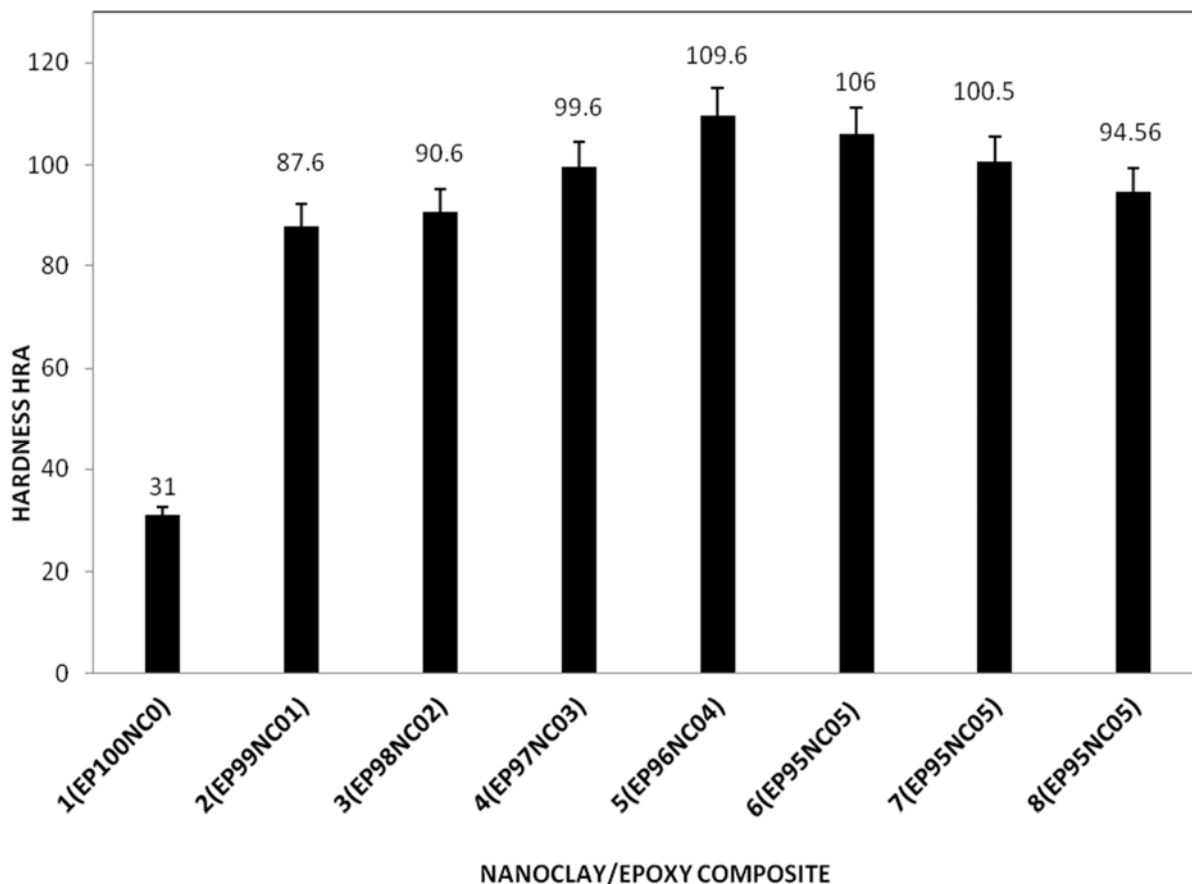


Figure 1: Effect of Nanoclay Loading on Hardness Property of Nanoclay/Epoxy Composite

The morphological images of the specimen obtained using Scanning Electron Microscopy (SEM) are represented in Plates A, B and C. The Scanning Electron Microscope (SEM) image in Plate A shows the SEM image of composite 5 (the optimum composite with the highest hardness value) with 4:96 wt. % nanoclay/epoxy content. From the image, it is deduced that the use of nanoclay particles reduced crack (fracture) initiation and growth and enhanced the hardness of the nanoclay/epoxy composite (Shehata *et al.*, 2019). Plate A showed proper, uniform and homogeneous dispersion/distribution of nanoclay with less void (Namdev *et al.*, 2023) an indication of good interfacial adhesion, good cohesion and surface association between the epoxy matrix and the nanoclay fillers, which is mainly responsible for the increase in the hardness of the composite (Sawsan *et al.*, 2023).

Plate B shows the SEM image of composite 8 (the composite with the lowest hardness value) with 7:93 wt. % nanoclay/epoxy content. The disproportionate dispersion of the nanoclay particles in the epoxy matrix can be observed. The image shows a heterogeneous

picture with characteristics of lumps and agglomerates due to poor cohesion between nanoclay particles and the epoxy matrix at high filler loading, which resulted in a decrease in the hardness value of the composite. The agglomeration led to the emergence of areas saturated with nanomaterials at the expense of other areas (Sawsan *et al.*, 2023). Plate C reveals the Image of the control sample (neat epoxy). This conforms to the works of (Marquis *et al.*, 2022).

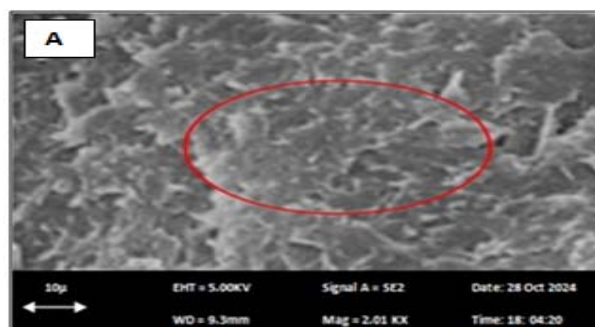


Plate A: SEM image of Composite 5 (96:4 wt %) epoxy/nanoclay content

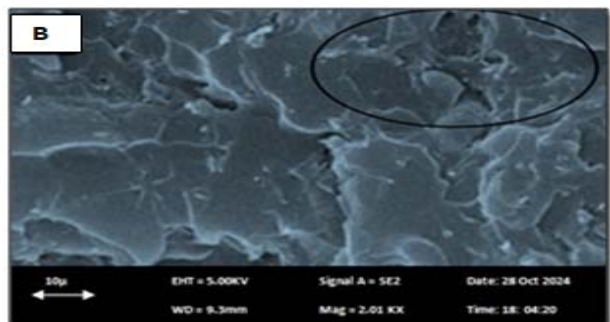


Plate B: SEM image of Composite 8 (93:7 wt %) epoxy/nanoclay content

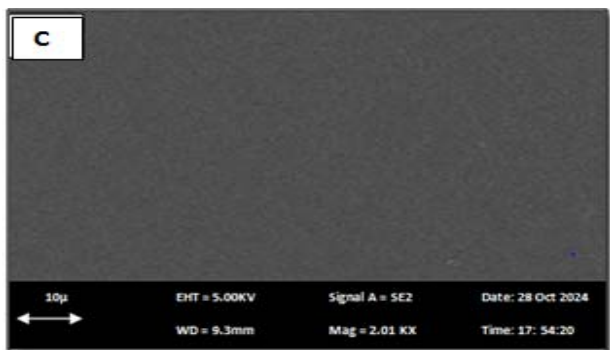


Plate C: SEM image of Composite 1 (control sample) cured epoxy material

See the circled parts of SEM images A, B, and C for lucidity. This affirms the reports of (Kusmono *et al.*, 2023), which reported that nanoparticles have the ability to enhance the satisfactory mechanical properties of polymer materials.

CONCLUSION

This study confirmed that the addition of nanoclay significantly enhances the hardness of epoxy composites. The optimum performance was observed at 4 wt.% nanoclay, which achieved a hardness value of 109.6 HRA—more than three times that of neat epoxy. SEM analysis showed that the improvement was due to uniform dispersion and strong interaction between the nanoclay and epoxy matrix. The enhanced composites are suitable for industrial and engineering applications such as flooring, brake pads, and protective coatings.

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